

# REPORT DOCUMENTATION PAGE

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| 13. ABSTRACT (Maximum 200 words)<br>The objective of this project was to acquire a X-ray diffraction spectrometer for the study of nanomaterials. In a current project supported by the Air Force Office of Sponsored Research, the WKU Materials Characterization Center (MCC) is conducting research on polymer/clay nanocomposites, with the intent of gaining a better understanding of the relationship between processing and the microstructure properties of the nanomaterials. The Center plans to use its current holdings and projects to establish a Nanomaterials Research Laboratory. Prior to this project, the available instrumentation included atomic force microscopy/Micro-TA, scanning electron microscopy, and transmission electron microscopy. However, these instruments can not provide all the necessary information for current and proposed projects, and there was a pressing need for an x-ray diffraction (XRD) system for microstructure analysis of nanocomposites. |  |   |  |   |  |
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**Final Performance Report**

**Acquisition of an X-ray Diffractometer for Nanotechnology Research**

**Research Grant F49620-01-1-0334**

**May 1, 2001 to April 30, 2002**

**Prepared by:**

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## 2. Objectives

The objective of this project was to acquire an X-ray diffraction spectrometer for the study of nanomaterials. In a current project supported by the Air Force Office of Sponsored Research, the WKU Materials Characterization Center (MCC) is conducting research on polymer/clay nanocomposites, with the intent of gaining a better understanding of the relationship between processing and the microstructure properties of the nanomaterials. The Center plans to use its current holdings and projects to establish a Nanomaterials Research Laboratory. Prior to this project, the available instrumentation included atomic force microscopy/Micro-TA, scanning electron microscopy, and transmission electron microscopy. However, these instruments can not provide all the necessary information for current and proposed projects, and there was a pressing need for an x-ray diffraction (XRD) system for microstructure analysis of nanocomposites.

Recently XRD has become an indispensable analytical technique for use in polymer/clay nanocomposite studies. X-ray diffraction can precisely measure atomic distances, d-spacings between clay layers, large-scale structure and long range order, and particle size and shape. The use of a high temperature attachment with XRD instrumentation allows the analysis of variation of microstructure and composition of nanocomposites with temperature, such as phase transformation and order/disorder transformations. The acquisition of the XRD system greatly enhanced the Center's capabilities in undergraduate and graduate education and fundamental research in nanoscience.

## 3. Status of Efforts

In 2001, a Thermo-ARL-SCINTAG X'TRA X-Ray Diffraction Spectrometer (XRD) was purchased from Thermo-ARL, Germany. The total cost of the system was \$163,643. Special features of this instrument include the capability of both wide-angle X-ray scattering (WAXS) and small-angle x-ray scattering (SAXS), and a high temperature chamber that can operate up to 1600°C both under vacuum and air conditions.

The ARL X'TRA XRD system contains a diffraction system with a Peltier detector, an M-series master processing unit (MPU), a high temperature chamber for vacuum to 1600°C, and a diffraction management system (DMSNT software) for data collection and analysis.

Detailed information about the XRD system configuration is as follows:

### (1) Diffraction System with Peltier Detector:

X-Ray protection cabinet;

- ◆ X-ray safe enclosure complies with all x-ray safety regulations, including safety interlocks and external control tower with warning lights and sounds.
- ◆ Leaded acrylic window allows view of goniometer and sample area.

- ◆ Large interior fluorescent light provides cabinet and goniometer illumination.
- ◆ Rear mounted. Large capacity, low noise airflow fan assures proper cooling.
- ◆ Left and right side 19" racks allow room for standard and optional accessories.
- ◆ Adjustable cabinet feet for exact leveling.

#### X'TRA vertical Theta (Theta wide angle goniometer):

- ◆ Flexible goniometer geometry adjustable between 360-540 mm diameter.
- ◆ High resolution digital servo drive system with optical encoder.
- ◆ Absolute encoder accuracy of  $\pm 0.0009$  degrees and precision of  $\pm 0.00025$  degrees.
- ◆ Flexible incident/diffracted beam slit system continuously adjustable between 0-10 mm via micrometer.
- ◆ Universal X-Ray tube tower accepts standard glass or ceramic X-Ray tube. Tube tower is mounted directly on the goniometer for maximum stability and ease of alignment.
- ◆ Universal single sample precision centerpost for rapid exchange of sample stages.

#### Thermoelectrically Cooled Si(Li) detector:

- ◆ Electronic discrimination of Cu K-beta and fluorescence with no loss of Cu K-beta intensity.
- ◆ Dual channel output for automatic deadtime correction. Detector output linear to at least 50,000 cps.
- ◆ 5 stage Peltier device for cooling detector crystal without need for liquid nitrogen. This eliminates thermal background in the detector.
- ◆ High vacuum metal:metal seals to prevent detector contamination.

#### (2) M-Series Master Processing Unit (MPU)

- ◆ Single board MPU, programmable with high-level language.
- ◆ PC mounted PCI parallel processor assuring high-speed parallel data transfer to PC memory.
- ◆ Shutter processor logic controls all fail-safe circuitry.
- ◆ Computer control of high voltage generator current/voltage and detector single channel analyzer.
- ◆ Simplified system status checks through software or through "on-board" status display lights.

#### 4kW solid state electronics:

- ◆ Computer-controlled voltage, adjustable between 8-60 kV in steps of 0.1 kV.
- ◆ Computer-controlled current adjustable between 0-80 mA in steps of 0.1 mA.

(3) Copper X-Ray Tube and Cooling System:

- ◆ Normal focus Cu X-ray tube rated for use at maximum of 2000 Watts.
- ◆ Includes short anode adaptor mount and four Be windows.
- ◆ Copper anode material.
- ◆ 2000 Watts at 60 kV & 33.3 mA maximum wattage
- ◆  $1.0 \times 10 \text{ mm}^2$  focus spot size.
- ◆ 3.5 liters/min minimum cooling water flow.

(4) Diffraction management System-DMSNT Software:

- ◆ Data Collection and Analysis software.

(5) High Temperature Chamber for Vacuum Operation to 1600°C;

- ◆ Temperatures up to 1600°C.
- ◆ 19" rack mount controller.
- ◆ Computer interface for use with ARL/Scintag's DMS/NT software package.
- ◆ The chamber includes a single thermocouple feed-through, single heater circuitry, one KF40 vacuum port and one KF25 vacuum port, mounting bracket for ARL/Scintag style goniometer systems.

The XRD spectrometer was fully installed and tested by the manufacturer in September, 2001. A two-day training course was also conducted at that time, including the basic instrument operation, data collection and analysis, and the utilization of JCPDS PDF2 database system. Both undergraduate and graduate students attended the instructional course.

XRD experiments were then conducted for an ongoing project entitled "A Study of the Thermal Stability, Degradation Mechanisms and Properties of Polymer/Organically Modified Layered Silicate Nanocomposites" (Grant F49620-00-1-0260). Polymer layered silicate (PLS) nanocomposites are a new class of materials with dimensions typically in the range of 1 to 100 nm. The ultra fine phase dimensions of the nanocomposites lead to their new and improved properties, when compared to their micro- or macro composite counterparts. These polymer layered silicate nanocomposites can attain a certain degree of stiffness, strength and barrier properties with far less ceramic content than comparable glass- or mineral- reinforced polymers. As such they are far lighter in weight than conventionally filled polymers; also they avoid many of the costly and cumbersome fabrication techniques, and can be prepared using traditional polymer processing technology instead.

Two distinct nanocomposite structures have been identified with layered silicates. Exfoliated or disordered hybrids retain little or no registry between the silicate layers, which are typically separated by as much as 5-15 nm. Intercalated hybrids, on the other hand, retain registry between the host layers, albeit with an expanded gallery height or distance between layers, which reflects the incorporation of polymer chains into the

structure. Intercalated hybrids represent ideal systems for studying polymers in confined environments. Irrespective of the fabrication route in the nanocomposite synthesis, two key factors are always considered in the PLS synthesis, including the miscibility between polymer and layered-silicates, and the interlayer spacing of the layered silicates which will decide whether the polymer chain can be incorporated into it. Since the natural behavior of layered silicates is hydrophilic, in order to render these hydrophilic layered silicates more organophilic, the hydrated cations of the interlayer in layered silicates can be exchanged with cationic surfactants such as alkylammonium or alkylphosphonium. The modified clay (organoclay) being organophilic, its surface energy is lowered and is more compatible with organic polymers. Considering the interlayer spacing, replacing the hydrated cations by ion-exchange with organic cations, such as more bulky alkylammonium ions, usually results in larger interlayer spacings allowing the polymer chain to penetrate into the interlayer.

XRD spectroscopy, therefore, plays an important role in the characterization of both organically modified layered silicates and the structure of polymer layered silicate nanocomposites. In the case of organically modified layered silicates, one of the examinations in whether the surfactant is truly intercalated into silicate interlayers is to measure  $d_{001}$  change before and after ion exchange process. The  $d_{001}$  spacing for pristine montmorillonite measured by XRD is 1.15 nm, and the  $d_{001}$  spacing for organically modified montmorillonite was greatly increased, ranging from 1.50 nm for trimethyldodecyl ammonium modified montmorillonite to 2.60 nm for dimethyldihydrogenated tallow ammonium modified montmorillonite. Depending on the chain length and architecture of surfactant, the degree of increase in the  $d_{001}$  spacing varies from sample to sample. However, the general trend is that the longer the alkyl chain length is, and the more the long alkyl chain surfactant possesses, the larger the  $d_{001}$  spacing the modified montmorillonite has. The detailed experimental results are summarized in Table 1.

In the case of polymer layered silicate nanocomposites, XRD spectroscopy was used to characterize the structure of PLSN – exfoliated or intercalated. For the nanocomposites sample with the intercalated structures, since the repetitive multilayer structure is well preserved, the interlayer spacing can be determined. The intercalation of the polymer chains usually increases the interlayer spacing, leading to a shift of the diffraction peak toward lower angle values. A typical XRD spectroscopy pattern for the intercalated Poly(methyl methacrylate)-montmorillonite nanocomposite is shown in Figure 1, where the  $d_{001}$  spacing is found around 4.10 nm, indicating that PMMA is intercalated into the montmorillonite silicate sheet. On the other hand, for the nanocomposite samples with the exfoliated structure, no more diffraction peaks are visible in the XRD diffractograms, either because of a much too large spacing between the layers (i.e. exceeding 8 nm in the case of ordered exfoliated structure) or because the nanocomposite does not present ordering anymore.

In summary, the XRD spectrometer was successfully installed and employed in various research projects. This spectrometer not only greatly enhances the Materials

Characterization Center's capabilities in undergraduate and graduate education, but provides much needed technical support for various research projects.

Table 1. Quaternary Ammonium Modified Montmorillonites.

| Sample | Surfactant   | d <sub>001</sub> |
|--------|--|------------------|
| ID     |  | (nm)             |
| MMT    | Pristine MMT   | 1.15             |
| 2044   | Trimethyl, coco quaternary ammonium chloride                         | 1.39             |
| 2047   | Trimethyl, dodecyl quaternary ammonium chloride                      | 1.45             |
| 2046   | Trimethyl, tallow quaternary ammonium chloride                       | 1.78             |
| 2048   | Trimethyl, octadecyl quaternary ammonium chloride                    | 1.82             |
| 2049   | Dimethyl, benzyl, dihydrogenated tallow quaternary ammonium chloride | 1.81             |
| 2043   | Dimethyl, dicoco quaternary ammonium chloride                        | 1.89             |
| 2042   | Dimethyl, dihydrogenated tallow quaternary ammonium chloride         | 2.39             |
| 2052   | Dimethyl, dioctadecyl quaternary ammonium chloride                   | 2.47             |

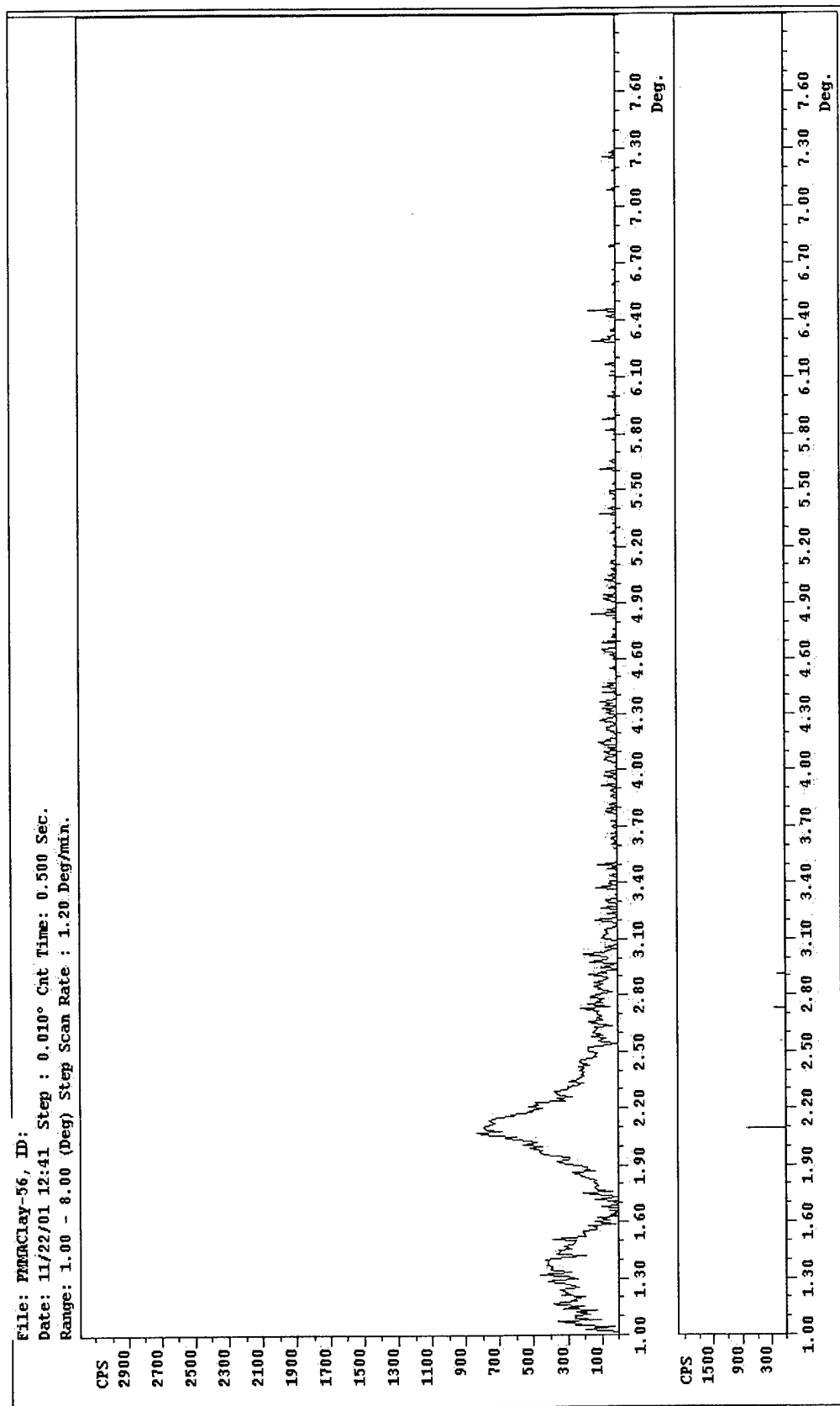


Figure 1. A typical XRD pattern for PLSN with intercalated structure.